

PATENT SPECIFICATION

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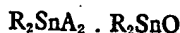
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 (72) Inventor JOHN RANDOLPH LEEBRICK



(54) SILICONE RUBBER COMPOSITION HAVING IMPROVED CURING CHARACTERISTICS

- (71) We, COSAN CHEMICAL CORPORATION, a corporation duly organized under the laws of the State of New Jersey having an office at P.O. Box 1042, Clifton, New Jersey, United States of America do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—
 10 A silicone rubber composition having improved curing characteristics which has incorporated as a curing catalyst 0.1—5% by weight, calculated on the weight of the silicone, of a Harada complex defined by the empirical formula



- wherein A stands for alkyl, containing from 1—8 carbon atoms and A is a carboxylic acid radical containing 1—22 carbon atoms. Also a method of making the silicone rubber composition so defined. The composition has a great variety of uses including application as coating, surfacing, insulating, sealing, molding and the like materials.

- Many systems are presently in use for the curing or vulcanizing of organosiloxane polymers, widely known as silicone rubber. Among these systems is the use of a catalyst comprising carboxylic acid salts of certain metals. One group of catalysts used commercially includes the organotin dicarboxylates, such as dibutyltin dilaurate.

- Although such catalysts have wide use commercially, they exhibit certain disadvantages, which make them unsuitable for many industrial applications. Among these disadvantages is their relatively long curing time, their corrosive action on metal surfaces, which makes them unsuitable for coating or encapsulating of electronic appliances, and their tendency to chain scissions, i.e., breaking of cross links between polymer chains, thus weakening the polymer structure of the silicone rubber.

It is, therefore, an object of the present in-

vention to provide improved organotin catalysts for silicone rubber.

It is a further object to provide a silicone rubber-catalyst composition which has a shorter curing time, which is non-corrosive, and which is free of chain scission.

The invention also provides a method for making a silicone rubber composition of improved curing characteristics.

Other objects and advantages of the present invention will become apparent from the following detailed description.

Catalysts heretofore used of the type described above have been prepared by reacting one mole of a dialkyltin oxide with two moles of a dicarboxylic acid, or by reacting one mole of a dialkyltin dihalide with two moles of a carboxylic acid in the presence of a base. The resulting organotin carboxylates contain varying amounts of free acid which, it was discovered, were partly the cause of the problems mentioned above.

The compositions according to the invention make use of organotin carboxylates having negligible amounts of free acid, and thereby provide a faster cure. Furthermore, the catalyst does not contribute to corrosion or chain scission.

The catalysts of the present invention are prepared by the reaction of one mole of dialkyltin oxide with one mole of a carboxylic acid. As mentioned above, the resulting basic organotin carboxylates contain negligible free acid. The rate of catalysis is faster than that of current commercial catalyst. The catalysts do not contribute to chain scission.

The improved catalysts may be defined by the empirical formula



identified in the literature as *Harada* complexes. R stands for alkyl, containing from 1 to 8 carbon atoms. Typical R groups may be methyl, ethyl, propyl, butyl and octyl. The preferred R group is methyl, although R may

also conveniently be butyl or octyl. A is a carboxylic acid radical containing 1 to 22 carbon atoms. Typical A groups are formate, acetate, propionate, butyrate, ethylene diamino-tetra-acetate, octoate, 2-ethyl-hexoate, pelar-gonate, decanoate, including neodecanoate, laurate, oleate and stearate. Preferred groups are the laurate, neodecanoate and oleate.

The Harada complexes are described in the literature in the following articles or abstracts of articles by Harada: Sci. Paper Inst. Phys. Chem. Research (Tokyo), 35, 290 (1939); Chem. Zentr.. (1939) II, 2912; Sci. Papers Inst. Phys. Chem. Research (Tokyo), 38, 146 (1940); Chem. Abstracts, 35, 2470 (1941); and Chem. Abstracts, 43, 4632 (1949). An excel-lent discussion of Harada complexes also ap-pears in the monograph by Luijten and Van Der Kirk, entitled Investigations in the Field of Organotin Chemistry, Published by the Tin Research Institute.

The catalysts may be used at concentrations of 0.1% to 5%, preferably at 0.5% to 2%.

In the following the invention will be more fully explained in a number of examples which are given, however, by way of illustration and not of limitation.

The first two examples relate to the pre-paration of the catalyst according to the inven-tion, whereas Examples 3—6 deal with curing effect on silicones.

EXAMPLE 1

164.7 g. (1.0 mole) of dimethyltin oxide and 282.45 g. (1.0 mole) of oleic acid are charged into an open reactor equipped with stirrer, heat source, and thermometer. The mixture is heated, while being thoroughly stirred at 120°C until all water is eliminated. Basic di-methyltin oleate is obtained as a light yellow moderately viscous product, which can be used directly for admixture with the silicone to be cured.

EXAMPLE 2

For the preparation of basic dibutyltin laurate, 248.8 g. (1.0 mole) dibutyltin oxide and 200.3 g. (1.0 mole) of lauric acid were used and treated as described in Example 1. The resulting product was directly used as catalyst.

EXAMPLE 3

To 50 g of RTV-60 (General Electric's room temperature vulcanizing silicone) is added 1 g. of a catalyst made according to Example 1 and the mixture is stirred thoroughly at room temperature.

In a similar manner, a composition is pre-pared with a commercial catalyst, viz., dibutyl-tin dilaurate.

The curing times are then compared at room temperature and the figures found are shown below.

Catalyst	Concentration %	Tack-free time, Minutes
Basic dimethyltin oleate	2	27 (tough cure)
Basic dimethyltin oleate	1.5	77
Commercial dibutyltin dilaurate	2	99 (fairly tough cure)

EXAMPLE 4

This example relates to curing at elevated temperature.

To 50 g. of LTV-602 (General Electric's elevated temperature vulcanizing silicone) is added 1 g. of the catalyst according to Example 1, and the mixture is stirred thoroughly.

The mixtures are then immersed in an oil bath at 100° C and gel times are noted. The results are shown below.

Catalyst	Gel time in minutes
Basic dimethyltin oleate	10
Commercial dibutyltin dilaurate	120

EXAMPLE 5

In a manner similar to the one described in Example 3, the curing effectiveness of basic dibutyltin laurate, the catalyst made as de-scribed in Example 2 is tested at room tem-perature and compared with the commercial catalyst dibutyltin dilaurate at room tempera-ture. The test results are shown below.

Catalyst	Concentration %	Tack-free time, minutes
Commercial Dibutyltin dilaurate	1	>180
Basic dibutyltin laurate	1	74

EXAMPLE 6

For curing at elevated temperature, a test was made similar to the one described in Example 4 wherein basic dibutyltin laurate was tested in comparison to the commercial catalyst dibutyltin dilaurate at 100° C. Gel time measured was markedly faster when the catalyst of the invention was compared with the commercial catalyst.

It should be understood that various fillers and pigments can be incorporated in the compositions according to the invention as is customary in this art, depending on the use for which the compositions are intended.

Due to the characteristics outlined above, the compositions lend themselves to a great variety of technical, industrial and other applications.

Due to the complete absence of free acid, they have proved to be of great value in all instances where articles are to be protected against corrosion, and as surfacing and coating materials in general.

For the same reason, they are very useful as packing and sealing materials between metal pipes and other metal parts.

Another field of application is that of molding materials and additives where their cold curing characteristics and short time of curing are of importance, for instance in dentistry.

These are just a few of the possible applications for the novel compositions, others will be apparent to those skilled in the art from the properties explained in the above specification.

WHAT WE CLAIM IS:—

1. A silicone rubber composition having improved curing characteristics, which has incorporated as a curing catalyst 0.1—5% by weight, calculated on the weight of the silicone, of a Harada complex defined by the empirical formula



wherein R is an alkyl radical containing from 1 to 8 carbon atoms, and R is a carboxylic acid radical containing 1 to 22 carbon atoms.

2. A silicone rubber composition according to claim 1, wherein the catalyst is basic dimethyltin oleate.

3. A silicone rubber composition according to claim 1, wherein the catalyst is basic dimethyltin laurate.

4. A silicone rubber composition according to claim 1, wherein the catalyst is basic dibutyltin oleate.

5. A silicone rubber composition according to claim 1, wherein the catalyst is basic dibutyltin laurate.

6. A silicone rubber composition according to claim 1, wherein the catalyst is basic dioctyltin oleate.

7. A silicone rubber composition according to claim 1, wherein the catalyst is basic dioctyltin laurate.

8. A method of making a cured silicone rubber composition which comprises mixing a silicone rubber compound with a Harada complex as defined in claim 1, in the amount of 0.5 to 2% by weight, at a temperature ranging from room temperature to about 100°C, and stirring the mixture thoroughly.

9. A silicone rubber composition having improved curing characteristics as claimed in claim 1 and substantially as hereinbefore described.

10. A method of making a cured silicone rubber composition as claimed in claim 8 and substantially as hereinbefore described.

CRUIKSHANK & FAIRWEATHER.

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XA - C1991-130350

XIC - C08L-009/00 ; C08L-083/04

AB - J03200872 An adherent silicone rubber compsn. which is a liquid and becomes an elastomer by curing comprises: (A) 100 pts. wt. of silicone base polymer and (B) 0.5-20 pts. wt. of polyisoprene and/or isoprene-butadiene copolymer.

- (A) is classified into three types depending on curing reactions, i.e., crosslinking by peroxide, polycondensn. and polyaddn. The first type is a combination of 100 pts. wt. of polydiorganosiloxane having at least two vinyl gps. and 0.05-15 pts. wt. of a peroxide like BPO or dicumyl peroxide. The second type is a combination of 100 pts. wt. of polydiorganosiloxane having OH gps. on both terminals, 0.1-20 pts. wt. of at least one curing agent like ethyl silicate or methyltrimethoxysilane and 0.01-5 pts. wt. of a curing catalyst like tin octate or dimethyl tin oleate. The third type is a combination of 100 pts. wt. of polyorganosiloxane having at least two vinyl gps. and 1-1,000 ppm of a curing catalyst like chloroplatinic acid or platinum black.

- USE/ADVANTAGE - The adherent silicone rubber compsn. is suitable as an adhesive of polyolefins like PE and PP. This compsn. has high tackiness, good wettability to polyolefins and excellent adhesion, due to (B) component. (5pp Dwg.No.0/0)

IW - ADHERE LIQUID SILICONE RUBBER COMPOSITION BASED POLY SILICONE POLYISOPRENE POLYBUTADIENE COPOLYMER

IKW - ADHERE LIQUID SILICONE RUBBER COMPOSITION BASED POLY SILICONE POLYISOPRENE POLYBUTADIENE COPOLYMER

NC - 001

OPD - 1989-12-28

ORD - 1991-09-02

PAW - (TSIL) TOSHIBA SILICONE KK

TI - Adherent liq. silicone rubber compsn. - based on poly:silicone and polyisoprene-butadiene] copolymer

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